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Analysis and characterization of plutonium in pyrochemical salt residues

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Abstract

Quantitative measurement of hydrogen produced during salt-catalyzed hydrolysis of plutonium in pyrochemical salt residues show that the metal is present in concentrations of 10 ± 5 mass%. The analytical method is based on stoichiometric reaction of metal with water to form plutonium monoxide monohydride (PuOH) and hydrogen. Results of a kinetic model developed to describe the observed time dependence of the hydrolysis rate shows that metal is present predominately as particles with essentially spherical geometries and diameters near 1 mm. The presence of smaller metallic particles cannot be verified or excluded. Plutonium concentrations measured for residues stored in different configurations suggest that a sizable fraction of the metal has oxidized during storage. Application of the hydrolysis method in determining concentrations and dimensions of metallic plutonium in other nuclear waste forms is proposed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Safe disposition of legacy residues formed during nuclear materials processing is essential and must be accomplished without placing workers, the public, or the environment at risk [1]. Various forms of residues containing approximately 26 metric tons were generated at several US Department of Energy Facilities, including Rocky Flats. Many of these materials contain plutonium in metallic or oxide forms and present a spectrum of potential hazards. Identification of material forms suitable for disposition is necessary.

Characterization of plutonium-containing residues is a challenging task that must be performed to determine if existing material forms are stable or if processing is required. Most residues are complex chemical mixtures derived by combining by-products from similar processing sources into a single category. Adequate characterization of such complex matrices is difficult, especially at facilities with limited analytical capabilities. Materials containing metallic plutonium are of interest because of their potential for pyrophoric initiation of reaction, large thermal excursion, and dispersal of radioactive particles. Analysis of materials containing metallic plutonium is unusually difficult because commonly available techniques such as gamma spectroscopy, calorimetry, and X-ray fluorescence are useful in defining the total plutonium concentration, but are unable to distinguish between different chemical forms of the element. A simple quantitative method for determining the content of metallic plutonium in residues is needed.

Pyrochemical salts containing plutonium metal are of concern because about 16 metric tons of those potentially pyrophoric residues exist at Rocky Flats [1]. Molten chlorides of sodium, magnesium, potassium and calcium were used as solvents for molten salt extraction, direct oxide reduction, and electrorefining processes [2]. After separation from the castings of purified metal,

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solidified salts containing residual plutonium were placed in metal cans, enclosed in plastic contamination barriers, and stored in several locations (drums, partially inerted gloveboxes, and in-line vaults) for more than a decade. The current chemical condition of these materials must be established in order to assess their hazardous potential. Residues from electrorefining (ER) are of special concern because these mixtures containing NaCl plus KCl or $CaCl_2$ and $MgCl_2$ constitute approximately 45% of the salt inventory and may contain relatively high concentrations of Pu with estimates ranging from 10 to 90 mass%.

An analytical method based on the generation of hydrogen by hydrolysis of plutonium in aqueous salt solution [3,4] has been developed in an effort to quantify the amounts of metallic Pu present in ER salt residues. Kinetic results for the hydrolysis reaction are applied in defining properties of the metal particles.

2. Experimental methods

Hydrolysis tests were conducted by placing samples of ER salts in water and measuring the quantities of hydrogen generated over time. The amount of Pu present in each sample is defined by the total amount of H_2 produced. The time dependence of the H_2 generation rate is used to derive information about the sizes, shapes and concentrations of plutonium particles in the salt residues.

The amounts of hydrogen generated by the room-temperature hydrolysis reaction were determined by measuring pressure–volume–temperature (PVT) data and H_2 concentration in accordance with US Department of Transportation Test Method 49-CFR 173-124, Appendix E. Samples (10.0 g) of coarse (<4 mm size) and milled residues were obtained directly from storage containers. When weighed samples were placed in a volume-calibrated 0.5 l glass reaction vessel with 50 ml of water, the resulting solutions were 1–2 M in Cl^-. The quantities of H_2 generated during 1 h intervals were determined over a 7 h period from PVT data from the H_2 percentage determined by pumping samples of the gaseous product into a combustible-gas analyzer calibrated for hydrogen by the Mg + HCl reaction. The analyzer does not discriminate between hydrogen and carbon monoxide, but the presence of CO is unlikely. More than 100 analyses of salt residues were performed on samples with differing storage histories.

Rates of hydrogen generation (R) were calculated for 1 h measurement intervals and are reported in units of standard liters of H_2 per kg of salt residue per hour. The standard liter is defined at 1.013 bar pressure and 273 K.

3. Results and discussion

3.1. Relevant physical and chemical properties

The samples of salt residue analyzed in this study were from loose material formed during break-out of metal products from the solidified salts and from milled residues. Results of efforts to determine the size distribution of salt particles in an average unmilled residue are shown in Table 1. The largest mass fraction resides in salt fragments with dimensions between 4 and 60 mm. Hydrolysis samples were taken from the fraction with sizes less than 4 mm and are not considered representative of the bulk salt. The Pu concentration may exceed that of bulk material because metal particles settled to the bottom of the molten salt phase and are concentrated at surfaces where loose material was formed by mechanical action.

The results in Table 1 also address the potential dispersal hazard posed by unmilled salt residues. Approximately 1 mass% of the residues is comprised of particles with geometric dimensions less than 10 μm, the size range of plutonium oxide particles that is considered potentially dispersible. However, since entrainment depends on both particle size and density as defined by the aerodynamic diameter [5], the potentially dispersible range includes salt particles with geometric dimensions up to 20 μm. The mass fraction of particles in the geometric size range less than 3 μm is an estimated value based on results suggesting that the size distributions of fine particles produced by fragmentation of brittle solids are similar with about 10% of the 10 μm fraction in the size range below 3 μm [6]. These results provide a basis for assessing the dispersal hazard presented by these residues, but the average specific activity of the salt phase is a function of the Pu concentration and the likelihood of entrainment depends on the size of the Pu particles and the density of the plutonium-containing salt residue.

Table 1
Distribution of particle sizes for an average unmilled salt residue[a]

Geometric dimension	Cumulative mass fraction
<3 μm[b]	0.001
10 μm	0.01
250 μm	0.08
4 mm	0.2
<60 mm	1.0

[a] The distribution is based on combined results obtained by mass and volume measurements and sieving, in addition to characterization of the fine-particle fraction by optical microscopy.
[b] As described in the text, the mass fraction of particles in the respirable size range less than 3 μm is estimated.

Quantification of the hydrolysis results depends on the chemistry of the reaction between plutonium metal and water. The $Pu + H_2O$ reaction is very slow, but markedly accelerated in salt solution. Placement of a plutonium-containing salt sample in water at 25°C results in rapid salt-catalyzed reaction of plutonium to form plutonium monoxide monohydride (PuOH) and hydrogen [3,4].

$$Pu(s) + H_2O(l) \rightarrow PuOH(s) + 1/2H_2(g). \quad (1)$$

This stoichiometric reaction proceeds until all the metal is consumed. At that point, the fine black PuOH product begins to hydrolyze with formation of a second oxide hydride of Pu(III) and additional hydrogen.

$$PuOH(s) + 2/7H_2O(l) \rightarrow 1/7Pu_7O_9H_3(s) + 4/7H_2(g). \quad (2)$$

For 1M solutions of several metal dichlorides, the average corrosion rate of plutonium according to Eq. (1) is 134 ± 59 mg Pu/cm^2 h at 23 ± 3°C in near-neutral solution.

Correlation of observed H_2-generation steps with Eqs. (1) and (2) is possible because of the sequential nature of the hydrolysis process [4]. In addition to PuOH and $Pu_7O_9H_3$, the solid products formed following immersion of Pu in chloride solution at 25°C are Pu_2O_3 containing Pu(III), members of the Pu_nO_{2n-2} ($n = 7$, 9, 10 and 12) homologous series containing fixed ratios of Pu(III) and Pu(IV), and PuO_2 containing Pu(IV). Identification of these products is possible because the curve describing the time dependence of the total moles of H_2 formed per mol of Pu (H_2:Pu) is comprised of linear constant-rate segments with distinct changes in slope at H_2:Pu ratios of 0.50, 1.07, 1.50, 1.71, 1.78, 1.80, 1.83 and 2.00. The binary oxide compositions present at ratios in the 1.50–2.00 range correspond to formation of the binary oxides existing in the praseodymium–oxygen system. Formation of PuOH and PuO_2 is verified by analysis of the respective solids present at the 0.50 and 2.00 ratios. These results demonstrate that hydrolysis of Pu proceeds by a sequence of equilibrium-controlled steps in which subsequent reaction of a solid product does not occur as long as solid reactant remains. Reaction of PuOH begins only after all Pu metal is consumed via Eq. (1).

The rate of hydrolysis according to Eq. (1) is a function of temperature, pH, chloride concentration, and surface area of the metal [7], as well as the chemical identity of the chloride salt [3]. Corrosion kinetics are not altered by alloying of the metal with gallium. The activation energy (25 ± 4 kJ/mol) and the strong sensitivity to pH are not factors in the hydrolysis tests conducted with near-neutral solutions at room temperature. The important considerations for evaluating hydrolysis data are the identity and concentration of the chloride salt and the surface area of the metal. R has an exponential dependence on salt concentration and varies by a factor of six for different dichlorides at 1M concentration. The areal dependence of R is an important consideration because of variations in surface area with size and geometry of the plutonium particles.

The amount of H_2 formed by Eq. (1) and information about the sizes and geometries of reacting metal particles is conveyed by the observed dependence of R on time (t). Resolution of the H_2-generation steps corresponding to Eqs. (1) and (2) is facile because the corresponding rate constants (93 ± 11 and 7.01 ± 0.05 mol H_2/mol Pu d) [3] defined by the H_2:Pu-t data differ significantly. Since the areal hydrolysis rate is constant at fixed temperature, pH, and salt concentration, the completion time for Eq. (1) is determined by the minimum dimension (thickness) of the metal particle. The shape of the observed rate-time curve is determined by geometry of the metal particle. If the particle is essentially two-dimensional (foil or sheet), the metal area and hydrolysis rate remain essentially constant during reaction and the completion point of Eq. (1) is indicated by a sharp change to a slower constant rate. If the particles are spherical, the hydrolysis rate progressively decreases over time as the metal surface area shrinks. In both cases, completion of Eq. (1) is marked by attainment of a relatively slow constant rate.

3.2. Hydrolysis of plutonium-containing salt residues

The hydrolysis reactions described by Eqs. (1) and (2) are both observed when samples of salt residue are placed in water. In all cases, the rate of H_2 formation is most rapid initially, but progressively decreases to a constant value over time as shown by representative results in Fig. 1. The amount of metal present in each sample is defined by the total quantity of hydrogen generated during the initial stage of reaction. The largest observed amount (7.42 l H_2/kg) corresponds to a Pu content of 16 mass% in the salt residue.

The rate–time data in Fig. 1 are empirically described by an exponential equation in which C and D are the pre-exponential constant and the time constant characteristic of the measurement.

$$R = Ce^{-Dt}. \quad (3)$$

As shown by the lower curve in Fig. 1, the rate of H_2 formation during some tests reaches a constant value after 5–6 h. Occurrence of Eq. (2) is suggested by continued generation of H_2 at a slow constant rate beyond that point. In other cases exemplified by the upper curve, R continues to decrease after 7 h, indicating that the hydrolysis of metal was incomplete when measurements were terminated. Attempts to obtain a better empirical relationship for the R–t data were unsuccessful.

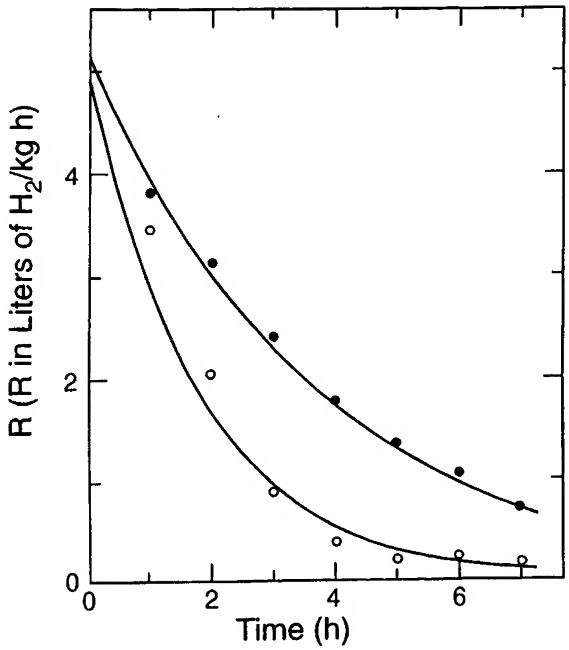

Fig. 1. Representative R–t data showing the exponential dependence of hydrogen-generation rate on time during hydrolysis of plutonium-containing salt residues. (Data from two measurements are indicated by open and filled circles.)

Results of fitting R–t data from 24 hydrolysis tests to Eq. (3) are listed in Table 2. Values of D appear in ascending order with the corresponding values of C and t_c, the time required for complete reaction of the metal. Values of t_c in excess of 7 h were obtained by calculating the point at which the change in the hydrolysis rate (dR/dt) is equal or less than 0.05 l H_2/kg h^2. Although the values of C vary randomly in a range bounded by 0.60 and 5.42 l H_2/kg h, a strong correlation is evident between D and t_c. For D values of 0.25 ± 0.05, 0.35 ± 0.05, 0.45 ± 0.05 and 0.55 ± 0.05 1/h, the experimental reaction times are 11.7 ± 1.1, 8.6 ± 1.2, 7.0 ± 0.7 and 5.4 ± 0.5 h, respectively.

The characteristic time constant and the time for complete reaction depend on properties of the plutonium particles and convey information about their shapes and sizes. The absence of Pu surface films, platelets, and other two-dimensional geometries is evident because the observed rate of H_2 generation varies continuously over time. Spherical geometries are suggested for metal particles by the curvature of the R–t data in Fig. 1. The utility of t_c in defining approximate dimensions of these particles is realized by transforming the areal Pu corrosion rate (134 ± 59 mg Pu/cm^2 h) in 2M Cl^- to the linear rate (R_L). For unalloyed Pu with a density of 19.8 g/cm^3, R_L is 0.07 ± 0.03 mm Pu/h. If the metal particles are assumed to be spherical and to corrode at this average linear rate, t_c values of 5 and 12 h correspond to

Table 2
Results obtained by empirically fitting rate–time data for reaction of plutonium in salt residues with water[a]

D (1/h)	C (l H_2/cm^2 h)	t_c (h)
0.190	3.46	14
0.211	2.81	13
0.228	1.33	11
0.274	5.17	11
0.318	4.07	10
0.313	2.44	10
0.324	4.84	10
0.328	2.65	9
0.340	4.87	8
0.353	2.37	9
0.354	2.44	8
0.382	4.42	8
0.384	2.57	7
0.385	2.14	7
0.424	0.60	8
0.428	3.31	7
0.441	2.45	7
0.467	2.48	7
0.477	2.84	6
0.524	4.48	5
0.556	5.01	5
0.577	2.59	6
0.585	4.38	5
0.588	5.42	5

[a] Data are fit to the equation R (mol H_2/cm^2 h) $= Ce^{-Dt}$. Values of t_c less than and greater than 7 h are derived by inspection of the data and by extrapolation of the fit curves, respectively.

times for complete reaction of Pu spheres with diameters of 1.2 ± 0.5 mm. These calculations, which define the largest sphere present in a sample, are based on assumptions that the corrosion rate is independent of the chemical identity of salt, that 2M Cl^- concentrations were present in all tests, and that corrosion kinetics are independent of the initial Pu particle size.

The presence of plutonium spheres with diameters on the order of 1 mm is consistent with the anticipated effect of surface tension on the formation of molten droplets during electrorefining and other pyrochemical processing. The characteristic diameter (d) of a liquid droplet is defined by the relationship involving the surface tension of liquid Pu (σ), the density of the liquid metal (ρ), and the gravitational constant (g).

$$d(m) = (\sigma/\rho g)^{1/2}. \quad (4)$$

Values of 0.55 N/m for the surface tension [9], 16,500 kg/m^3 for the liquid density [10], and 9.8 m/s^2 yield a diameter of 1.8 mm. Since the Pu particles formed while the metal and the salt were molten, it is reasonable for them to have the same spherical shape and diameter that existed prior to solidification of the salt. As discussed later in this section, extant particle diameters are

expected to be smaller than initial values because of oxidation during storage.

The emerging picture of the salt residue is that plutonium exists predominately as relatively large spherical particles in the salt matrix. Although a distribution including relatively small (10–500 μm size) metal particles might form during cooling after pyrochemical processing, formation of new particles is not anticipated because precipitation of metal at existing metal droplets is more likely than nucleation. Rate–time data show that one or more relatively large particle was present in each of the analytical samples. That observation alone suggests that the particle distribution is abnormal and that the reactivity of plutonium is dominated by the behavior of large particles.

Average results for residues with different storage histories in Table 3 indicate that metal particles have been partially oxidized during storage and that the extent of oxidation is strongly dependent on the history of the material. The lowest concentration of Pu is observed for salt residues milled prior to storage in drums. In addition to degrading the barrier of salt surrounding the metal particle and facilitating oxidation, milling of the salts probably produced a more homogeneous material with an average metal concentration less than that of loose material from unmilled residues. On average, the Pu content of unmilled residue stored in drums is 15% lower than that for similar materials stored in partially inerted gloveboxes, implying that Pu has been partially oxidized during storage. The reduction in metal content of milled residues suggests that about 65% of the plutonium has oxidized. If the initial diameters of the Pu sphere were 1.8 mm as suggested by calculation, their radii may have been reduced by as much as 0.4 mm, a change corresponding to 80% oxidation. A large extent of reaction is consistent with X-ray diffraction data showing that the concentration of PuO_2 in localized regions of the ER salt is about 20% of the non-metallic material [8]. Since partial oxidation of material store in gloveboxes is likely and tends to offset possible effects of homogenization during milling, an intermediate value of 30–40% is considered a realistic estimate of sample oxidation.

Observation of plutonium concentrations on the order of 10 mass% are consistent with process knowledge of ER salts and with reports that the metal is present as shot [1]. Although results obtained by direct evaluation of experimental data are instructive, a definitive determination of residue properties is needed for adequate assessment of the hazardous potential posed by these materials. This objective and confidence in our interpretation of results is achieved by modeling kinetic behavior of hydrolysis reaction.

3.3. A kinetic model for hydrolysis of plutonium

A quantitative kinetic model for hydrolysis of plutonium has been developed to more accurately define specific properties of plutonium particles in salt residues. The model quantifies behavior of plutonium particles over a range of conditions relevant to the hydrolysis tests. Results are applied in defining the geometry and determining dimensions of Pu particles in the salt residues. In concept, the model defines the time dependence of the hydrolysis rate of a metal particle with a specific geometry over possible ranges of linear corrosion rate and initial particle dimension. Variations caused by solutions with different chloride concentrations and different salt compositions are accommodated by calculating kinetic behavior for a matrix of linear corrosion rates and particle sizes. The model also yields values of t_c by defining the time period required for complete reaction of particles at different conditions. The model is validated and particle dimensions are determined by identifying conditions at which the observed correlation of D and t_c in Table 2 is correctly predicted.

The quantitative model uses an iterative method to calculate the extent of reaction for a single plutonium particle during a selected time increment. For the present evaluation, the plutonium particle is assumed to be spherical and the rate of hydrolysis (R_n in mol H_2/sphere h) during each iteration (n) of the calculation as defined by particle radii at the beginning (r_{n-1} in mm) and the end (r_n in mm) of the increment and by the time at the beginning (t_{n-1}) and end (t_n) of the increment.

$$R_n = 4\pi\rho_{Pu}\nu(r_{n-1}^3 - r_n^3)/3\mathrm{MW}_{Pu}(t_n - t_{n-1}). \tag{5}$$

The density of unalloyed Pu at room temperature (ρ_{Pu}) is 0.0198 g/mm^3, the stoichiometric ratio relating moles

Table 3
Plutonium concentration in salt residues stored at different conditions

Residue history	H_2 generated[a] (l/kg)	Pu concentration[b]	
		Mass%	Vol. %
Milled, drum storage	1.8	3.4	0.37
Unmilled, drum storage	4.1	7.2	0.82
Unmilled, glovebox storage	4.8	10.2	1.2

[a] Quantities of H_2 generated are average values obtained from measurements with samples from several sources of each material type.
[b] Pu concentrations are calculated using Eq. (1).

of H_2 to moles of Pu (v) is 0.5, and the molecular weight of plutonium (MW_{Pu}) is 239 g/mol. At $t = 0$, $r = r_0$, the initial radius of the spherical particle. Values of r_n are defined by the diameter at the beginning of each time increment, R_L in mm/h, and the length of the time increment in hours.

$$r_n = r_{n-1} - R_L(t_n - t_{n-1}). \quad (6)$$

The value of t_c for a spherical particle is given by r_0/R_L.

Rate–time behavior calculated for two conditions via the quantitative model are compared with experimental data in Fig. 2 using the logarithmic form of Eq. (4).

$$\ln R = \ln C - Dt. \quad (7)$$

Calculated rate–time results for corrosion of a 1 mm-diameter sphere at 0.05 mm/h (filled circles) are in excellent agreement with experimental data (open circles). The value of C is a function of the corrosion rate and the Pu concentration in the sample, and was arbitrarily scaled for comparison. Calculated results for corrosion of a 1 mm-diameter sphere at a corrosion rate of 0.09

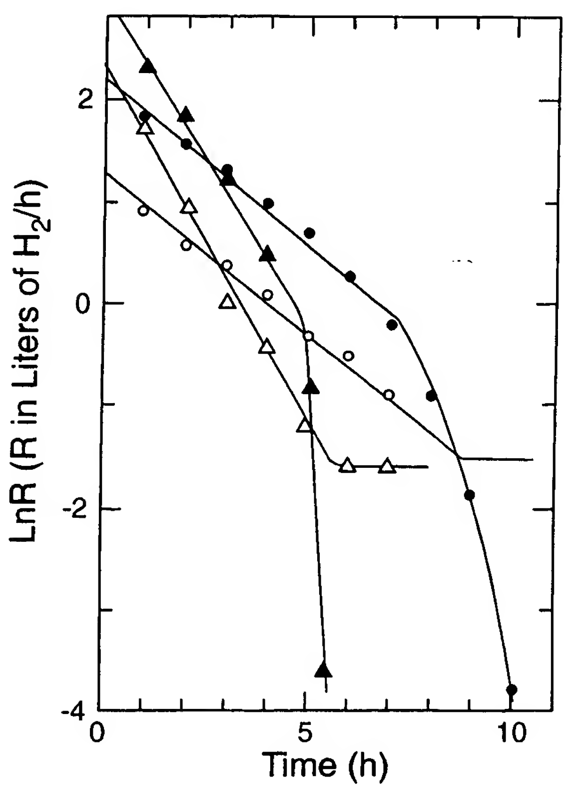

Fig. 2. Comparison of calculated and experimental $\ln R$–t curves for hydrolysis of two plutonium-containing salt residues. (Calculated data for reaction of 1 mm-diameter spheres at 0.05 and 0.09 mm/h are shown are shown by filled circles and filled triangles, respectively. Experimental data are shown by the corresponding open symbols.)

mm/h (filled triangles) are also compared with experimental data (open triangles). The shapes and the slopes (D values) of the curves and the time periods for complete reaction calculated assuming a spherical geometry for the plutonium particles closely match experimental observations. Rate–time behavior was not closely predicted by results of parallel calculations for rectangular geometries. The terminal shapes of the curves differ because the calculated curves only consider the reaction of Pu according to Eq. (1), not continuing reaction by Eq. (2). Whereas the calculated curves show that R approaches zero at t_c, the experimental curves show that H_2 continues to form at a slow constant rate. Calculations for the upper curve in Fig. 2 show that hydrolysis is more than 97% complete after 7 h, even though reaction continues for an additional 3 h. These results validate the model and suggest that plutonium particles in ER salts are essentially spherical.

Dimensions of the plutonium spheres in the salt residue are defined by values of the time constant and the complete time period, calculated for a matrix of corrosion rates and initial diameters. The results in Table 4 show that the calculated sets of D and t_c match experimental results only for r_0 values of 1 mm. Values of D appearing in Table 2 are observed at other conditions, but the associated values of t_c are not in agreement. The unique correspondence of calculated and observed kinetic parameters indicates that the metal particles are spherical with diameters of 1.0 ± 0.2 mm.

The presence of spheres with diameters significantly less than 1 mm cannot be excluded by the results in Table 4. This possibility or the presence of magnesium metal formed during processing is suggested in Fig. 1 by positive deviation of measured H_2 generation rates from the lower curve during the first 2 h of the analysis. Such behavior is observed for about half of the rate–time curves listed in Table 2. That observation suggests that the behavior is random and unrelated to the presence of Mg formed by electrolytic reduction. Although unlikely, Pu particles in a distribution of sizes may have formed in addition to spheres with large diameters. Normal mass and particle distributions for plutonium oxide with sizes in the 0.25 μm to 3.0 mm range show that the fraction with dimensions greater than 0.6 mm includes only 0.003% of the particles, but 45% of the mass [6]. Since the amount of Pu is apparently reduced by 30–40 % during storage, particles with initial diameters less than 0.3–0.6 mm, as well as films of metal that might have deposited on surfaces, were most likely oxidized during storage. If a normal distribution of metal particles existed in the salt residues after processing, only a skewed distribution of residual cores from relatively large particles remains.

The limited effect of relatively small particles on kinetic behavior is demonstrated by results of an $\ln R$–t calculation for a 1:1 mixture of spheres with diameters

Table 4
Calculated values of D and time periods for corrosion of spherical Pu particles with different initial diameters at different linear rates in salt water[a,b]

Linear corrosion rate (mm/h)	Calculated values of D and t_c (1/h) and (h) (initial sphere diameter in mm)		
	0.5	1.0	2.0
0.03	0.19 (8.3)	0.15 (17)	0.08 (30)
0.04	0.32 (6.2)	0.27 (12)	0.11 (25)
0.05	0.39 (5.0)	0.33 (10)	0.13 (20)
0.06	0.51 (4.1)	0.39 (8)	0.20 (17)
0.07	0.66 (3.6)	0.50 (7)	0.24 (14)
0.09	0.78 (2.8)	0.60 (6)	0.37 (11)

[a] Calculated values of D (in reciprocal hours) are listed for each condition with the corresponding reaction periods (in hours) given in parentheses.
[b] The experimentally measured values of D and corresponding values of t_c in parenthesis are 0.25 (11.7), 0.35 (8.6), 0.45 (7.0) and 0.55 (5.4).

of 0.5 mm (1.3 mg Pu/sphere) and 1.0 mm (10.4 mg Pu/sphere). The value of D derived for corrosion of this mixture at 0.06 mm/h is 0.40, a result that does not differ significantly from the 0.39 value calculated for a sample containing only 1.0 mm diameter spheres. Small metal particles may be present in the salt residues, but the kinetic behavior during hydrolysis is clearly dominated by reaction of large particles.

3.4. Modeling of plutonium concentrations in salt residues

The scope and utility of the kinetic model are extended by calculating values of the pre-exponential constant defining the initial hydrolysis rate. Since the magnitude of C depends on the corrosion rate (chemical identity and concentration of salt) and the concentration of plutonium, as well as the size and geometry of the metal particles, this exercise provides an opportunity to assess the internal consistence of the model, and to validate its predictions. If residual metal is present as 1 mm-diameter spheres, calculated and experimental values of C should agree in the range of bulk plutonium concentration determined by measurements of total H_2 generation, and in the range of corrosion rates indicated by experiment and modeling.

Certain properties of the salt residue must be estimated in order to calculate values of C. These data are presented in Table 5 for a range of plutonium concentration extending up to 90 mass%. The average residue densities are estimated assuming a density of 2.1 g/cm^3 for the ER salt phase and ideal behavior of the composite system. The number of 1 mm-diameter spheres present in a cubic centimeter of salt is surprisingly large. For residues containing 10 mass% Pu, a typical 10 g sample used for hydrolysis contained 85 spheres. At 90 mass% Pu, the 1 mm-diameter spheres are not randomly distributed in the salt matrix, but must be present in cubic or closest-packed arrays with surfaces touching adjacent spheres.

Pre-exponential constants calculated for a range of corrosion rates and plutonium concentrations are presented in Table 6. Plutonium metal was assumed to be present only as 1 mm-diameter spheres. Values of C were derived by calculating hydrolysis rates for the first hour and extrapolating to zero time using the median value of D (0.4 1/h) predicted by the model. Reference to Table 2 shows that experimental values of C lie in the range between 1 and 5 l H_2/kg h. In Table 6, these values of C are centered at a Pu concentration of about 10 mass%. The presence of slightly higher concentrations cannot be excluded for low corrosion rates, but values approaching 30 mass% are highly unlikely. Plutonium concentrations on the order of 90 mass% are not credible, considering that the samples used for

Table 5
Calculated properties of salt residues containing different concentrations of 1 mm-diameter plutonium spheres[a]

Plutonium concentration		Average density (g/cm^3)	Spheres per cubic centimeter of residue
Mass%	Vol. %		
10	1.1	2.3	19
30	4.3	2.9	83
50	9.6	3.8	185
70	19.8	5.6	380
90	48.8	10.7	938

[a] Plutonium concentrations and residue densities were calculated assuming ideal behavior of the salt and plutonium phases.

Table 6
Calculated values of C for possible ranges of corrosion rate and plutonium concentration in the salt residue

R_L (mm/h)	Calculated R (μm H_2/sphere h)	C calculated at specified Pu concentrations[a] (l H_2/kg h) (Mass% Pu)			
		10	30	50	70
0.03	3.7	2.2	3.9	5.5	8.6
0.04	4.8	2.4	4.6	6.7	10.8
0.06	6.9	2.8	5.9	9.0	12.0
0.09	9.8	3.3	7.8	12.2	20.6

[a] Values of C are defined by summing the calculated value of R for the initial hour of reaction and 1.5 l H_2/kg h, the median difference between R at $t = 0$ and $t = 1$ h.

hydrolysis tests probably contained higher-than-average metal concentrations. The remarkable agreement between measurement and prediction affirms the validity of the kinetic model and the accuracy of the results.

An effort has also been made to determine if calculation of pre-exponential constants might resolve uncertainties about the presence of plutonium particles with dimensions less than 1 mm. Values of C were determined for hydrolysis of residues containing 10 mass% Pu at a rate of 0.06 mm/h. For each calculation, Pu was assumed to be present as spheres with a single diameter. Values of C obtained for diameters of 0.1, 0.2, 0.5 and 1.0 mm are 6.0, 5.6, 3.0 and 2.8 l H_2/kg h, respectively. These results demonstrate that small particles contribute to the hydrolysis rate, but the change is insufficient to distinguish the kinetic effects of small particles from those arising from experimental variation.

4. Conclusions

Hydrolysis measurements on ER salts stored at Rocky Flats show that plutonium is typically present in concentrations of 10 ± 5 mass%. The existence of residues with plutonium concentrations above 30 mass% seems unlikely and the possibility of concentrations near 90 mass% is not considered credible. Results for salts stored in different configurations indicate that a sizable fraction of the metal initially present has been oxidized during storage. Evaluation of kinetic data shows that plutonium exists as spheres with diameters of approximately 1 mm. Although the presence of smaller particles cannot be confirmed or excluded, strong evidence for their existence is not observed. Reactivity of plutonium metal in the salt residue is determined by the behavior of large spherical particles.

Results of this study demonstrate that hydrolysis is a simple, effective and inexpensive method for quantitatively determining the concentration of plutonium metal in nuclear waste forms. Analysis of such materials is often difficult because of the complex chemical nature of most residues and the low concentration of plutonium. The method readily overcomes these difficulties because the chemistry is well defined, the measurement of H_2 is facile and sensitive if PVT methods are coupled with mass spectroscopy, and samples can be sufficiently large that they yield reliable results. Uncertainties associated with the chloride concentration in this study are not encountered in applications where soluble salts such as chloride and nitrate are absent. Likewise, other active metals (alkali metals, alkaline earths and lanthanides) are not normally present. Measurements are facilitated by using a standard chloride solution with the corrosion rate calibrated against plutonium.

Our analysis of kinetic data for plutonium-containing salt residues shows that important properties of plutonium-containing residues can be determined by modeling kinetic behavior. Derivation of information about the size and shape of metal particles is possible. The success of kinetic modeling may be limited for materials in which plutonium is present in broad geometric ranges, but minimum dimensions of the largest metal particles are readily defined.

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